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(54) Title: LASER MARKING PROCESS

(57) Abstract: Thin, flexible plastic films, of the type used for the packaging of foodstuffs, may be printed using a laser marking technique by printing a layer or layers comprising a laser sensitive material and an ink so that heating of the laser sensitive material by absorption of laser radiation burns the ink selectively, so causing markings to appear.

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## LASER MARKING PROCESS

### FIELD OF THE INVENTION

5 [001] The present invention relates to a laser marking process for use on thin flexible plastic films of the type commonly used for the packaging of various types of foodstuffs, and especially to such a process using an ink which contains or is associated with a laser sensitive material.

### BACKGROUND OF THE INVENTION

10 [002] Many types of foodstuffs, for example snacks, confectionery, dry and frozen food, etc., are packaged in wrappings composed of thin flexible films of plastic materials. Although most of the printing on such wrappers can be done well in advance of use of the packaging, some, such as "use  
15 by" or "best before" dates, of necessity, must be printed soon after or soon before the foodstuff is packaged. There are, of course, many printing methods known, but none is completely satisfactory for this purpose. Desirably, the printing should be of the same quality as that of the rest of the printing on the wrapper. It should also be economical and be capable of being printed at the site where the food is packaged, as well as at the site where the rest of the wrapper is printed. Moreover,  
20 because the date will change every day, and it may also be necessary to accommodate other changes, for example to deal with products of varying shelf lives, it should be easy to change the content of what is printed, preferably via software in a computer-controlled printing operation. Where the contents of the packaging are fragile, if the printing has to be done afterpackaging, it is also essential that the printing should not involve any impact or any other form of applied pressure. Finally, and of  
25 great importance, the printing should be indelible under normal conditions of use. Most printing methods currently used for the application of such markings as "use by" or "best before" dates fail to achieve several of these desiderata. Similar requirements also apply to bar codes, which often have to be printed as a separate exercise from the main printing of the packaging.

30 [003] We have now discovered that a laser marking technique can achieve all of these desired aims most effectively.

[004] Laser marking of plastics materials is now well known [see, for example, "Laser Marking" by Paul D. Hartung, Chapter 17 of "Plastics Finishing and Decoration" edited by Donatas Satas, published by Van Nostrand Reinhold Co., New York, 1986]. It is a valuable method of marking which has found many applications. Its advantages include: the laser does not directly  
35 contact the item to be marked, and so there is no mechanical wear, neither is there any impact on the contents of the packaging;

it allows extremely small characters or symbols to be drawn; accurately and legibly, markings can be made at extremely high speeds; lasers are extremely reliable and require minimal maintenance, and other moving parts on the marking system are limited.

[005] In the past, most proposals for the use of laser marking have involved using the laser to remove material thermally or carbonise the polymer from a solid object composed of a resin, polymer or other laser sensitive material and so form a mark or impression on the object. Examples of such processes are described in US patents No. 5,928,780; 5,977,514; and 6,214,917, and in manufacturers' literature such as that issued by Merck KgaA ("Iridin®LS for the laser marking of plastics", June 1997). Such processes have the disadvantage that the plastic materials chosen for this use have to be restricted to those susceptible to thermal removal in this way. This can restrict the choice of materials and so may not be useable for some purposes. Moreover, this technique may result in localised thinning and weakening of the plastic substrate, which would be undesirable or unacceptable in wrappers for foodstuffs and many other materials.

[006] Another laser marking technique comprises using a laser to remove thermally a covering layer, thereby exposing a lower layer of a different colour from that of the covering layer, so providing visible markings. An example of such a process, for the marking of optical fibres or electric cables, is described in US Patent No. 5,111,523.

[007] A further laser marking method employs the heat generated by laser radiation striking a substrate to cause a change in the colour of a thermosensitive material, as described, for example, in US Patent No. 5,608, 429.

[008] There has also been a proposal for using the ability of a laser to change the colour of an ink containing a non-black inorganic lead compound to black, thereby forming a black mark on an object such as a printed circuit board, as described in US Patent No. 5,035,983. However, the use of a lead compound in these inks would not be acceptable for food use, as is envisaged by the present invention.

[009] Another type of laser marking process uses thin aluminium layers which are deposited by vacuum evaporation. Because these absorb in the range of the Nd:YAG-radiation, such aluminium layers can be removed by laser radiation. This can be used to remove coloured ink layers, printed on the aluminium layer or to make contrast forming layers visible, as described in US Patent No. 6,066,437. For this kind of laser marking, aluminium-coated films are necessary, which are expensive and the deposition of the aluminium requires specialised equipment, which means that it often cannot be done or cannot be done economically at the site where the packages are printed.

[010] It is also known to mark paper and cardboard by using the heat generated by a laser for the selective thermal removal of some of the ink applied to the surface thereof.

[011] Laser ablative imaging methods are also known in which a donor sheet containing a material which absorbs at the wavelength of the laser and a dye (rather than the pigment necessary in the present invention) is irradiated with a laser. The absorbing material converts the laser energy to heat, which is transferred to the immediately proximate dye. The dye vaporises and is transferred to the receptor, which is the material to be printed. Methods of this type are disclosed in GB 2083726.

[012] In European Patent application No. 0 756 942A1 (and corresponding US Patent No. 5,633,118) laser ablative imaging methods are disclosed in which layers including water-soluble infra-red (IR) absorbing dyes are ablated in selected areas to expose an underlying hydrophilic dye-receiving layer; this underlying layer is then treated with aqueous ink to provide a colour contrast with unexposed areas. These methods are suitable for the production of optical masks, monochrome transparencies, and the like.

[013] Other disclosures relating to the use of IR absorbing dyes in laser ablative imaging include US Patent No. 5,330,876, which discloses a dye layer comprising an image dye and an IR absorbing dye dispersed in a high molecular weight binder; and US Patent No. 5,576,268, which discloses a similar dye ablative recording element in which the support is a microvoided composite film.

[014] However, none of these prior proposals has addressed the question of applying a marking by means of a laser to a thin flexible film of a plastic material, such as is commonly used for the wrapping of foodstuffs.

## SUMMARY OF INVENTION

[015] In its broadest aspect, the present invention consists in a process for marking a flexible plastic material using a laser, which process comprises the steps: applying to a surface of a substrate comprising said flexible plastic material in one or more layers an ink in association with a laser sensitive material; drying the ink; exposing portions of the ink to laser radiation at a wavelength to which said laser sensitive material is sensitive so that laser radiation absorbed by the laser sensitive material heats and removes thermally the ink or causes the ink to change colour, so as to cause markings to appear on the exposed portions.

## DETAILED DESCRIPTION

[016] The expression "in association with" is here defined to mean that the ink and the laser sensitive material are in sufficiently close physical proximity that the heat induced in the laser

sensitive material by the laser radiation is sufficient to cause the thermal removal of the ink. The laser sensitive material and the ink may be applied in separate layers or together in one composition.

[017] In a further embodiment, the present invention consists in a process for marking a flexible plastic material using a laser, which process comprises the steps:

5 applying to a surface of a substrate comprising said flexible plastic material a laser sensitive material which is or is associated with a material that generates gas on heating; coating the laser sensitive material with a gas-impermeable layer; exposing portions of the laser sensitive material to laser radiation at a wavelength to which said laser sensitive material is sensitive so that laser radiation absorbed by the laser sensitive material heats and causes gas to be generated, so as to form raised  
10 markings to appear on the exposed portions.

[018] If desired, other layers, such as inks, non-pigmented coatings or varnishes, similar to the above-mentioned layers, or of other materials, as described in more detail below, may be applied to the coated substrate obtained as described above, either before or after exposure to the laser radiation.

15 [019] The layer of ink or layers of ink and laser sensitive material referred to above may cover the entire surface of the substrate, if desired. However, it is a benefit of the present invention that they need not do so. Thus, the layers may, if desired, cover only that portion or those portions of the substrate on which markings are subsequently to be printed, and they may be applied by conventional printing processes with considerable accuracy. For example, if the markings to be  
20 printed are "use by" or "best before" information, a single patch of the coating layers may be applied to the substrate in the position where this information is to be inserted. Alternatively, the invention is equally applicable to the printing of statutory information, which may vary from country to country and/or which may need to be in different languages for different countries. In this case, several patches of ink/varnish and laser sensitive material may need to be applied. Similarly, bar codes can  
25 be marked on areas that have been selectively coated with laser sensitive material.

[020] When the laser sensitive material is exposed to the laser radiation, it absorbs the energy of the radiation, becomes hot and generally removes the layer containing it and any other layers above it by thermal action. It therefore follows that the ink or non-pigmented coating should burn, degrade, evaporate or otherwise be thermally removable at a temperature to which the laser heats the  
30 laser sensitive material. The majority of inks and coatings currently available will do so, and so the selection of an appropriate ink or coating is not a difficult task.

[021] Several laser systems are commercially available, including excimer, Nd:YAG, frequency doubled Nd:YAG, frequency tripled Nd:YAG, helium, neon and CO<sub>2</sub> systems. In practice, the most readily available systems, and those preferred for use in the present invention, are

the CO<sub>2</sub> and Nd:YAG [neodymium (dopant): yttrium, aluminium, garnet] laser systems. The construction and use of such laser systems is well known.

[022] In general terms, the laser sensitive material is a material which can convert the energy of the laser radiation to thermal energy. The nature of the laser sensitive material used in the present invention will depend on the laser system chosen, as is well known in the field of laser making. For example, if the laser is of the CO<sub>2</sub> type, which operates at a wavelength of 10600 nm, the laser sensitive material is preferably: mica or metal oxide-coated mica particles, such as those sold by Merck KGaA, Darmstadt, Germany under the trade names Iriodin LS 800, Iriodin LS 805, Iriodin LS 810, Iriodin LS 830, Iriodin LS 835 or Iriodin LS 850, or those sold by EMI (EMI Industries, Inc. Hawthorne, New York, USA) under the trade names Laser Flair LS 800, Laser Flair LS 805, Laser Flair LS 810, Laser Flair LS 830, Laser Flair LS 835 or Laser Flair LS 850; aluminium powders, such as that sold by Silberline (Silberline Ltd., Leven, Scotland) under the trade names Silvet LR10, Silvet LR20, Silvet LR30, Silvet ET917, or Silvet ET1630, that sold by Eckart (Eckart GmbH & Co. KG, Fürth, Germany) under the trade name Ultrastar GX 2550, that sold by Wolstenholme (Wolstenholme International Ltd., Darwen, Blackburn, England) under the trade name Metasheen 1015 or that sold by Eckart under the trade name Rotosafe 751 or Rotosafe 700; carbon black, such as that sold by Degussa (Degussa AG, Frankfurt, Germany) under the trade name Printex XE2, Printex 3 or Printex L or that sold by Avecia (Avecia, Manchester, England) under the trade name Pro-Jet 900 NP Bx2005; kaolin and other silicates; titanium dioxide; and calcium carbonate.

[023] On the other hand, if the laser is of the Nd:YAG type, which operates at a wavelength of 1064 nm, the laser sensitive material is preferably: mica or metal oxide-coated mica particles, such as Iriodin LS 820, Iriodin LS 825, Iriodin LS 830, Iriodin LS 835 or Iriodin LS 850 (all ex Merck), or Laser Flair LS 820, Laser Flair LS 825, Laser Flair LS 830, Laser Flair LS 835 or Laser Flair LS 850 (all ex EMI); aluminium powders, such as Silvet LR10, Silvet LR20, Silvet LR30, Silvet ET917, or Silvet ET1630 (all ex Silberline), Ultrastar GX 2550 (ex Eckart), Metasheen 1015 (ex Wolstenholme) or Rotosafe 751 or Rotosafe 700 (both ex Eckart); carbon black, such as Printex XE2, Printex 3 or Printex L (all ex Degussa) or Pro-Jet 900 NP Bx2005 (ex Avecia); titanium dioxide; and calcium carbonate.

[024] It is also possible to use a combination of laser sensitive materials such that any one of several laser types would be effective in marking according to the process of the present invention.

[025] Other laser systems may be able to use some of the above laser sensitive materials or may use others. However, these materials are well known to those skilled in the art.

[026] There is no particular restriction on the nature of the ink used in the present invention, and any ink known for use in the printing of flexible plastic films may be used, subject only to the

restriction, as explained above, that it should be capable of being removed by the heat generated in the laser sensitive material by the laser radiation. Preferred examples of such inks include those comprising: nitrocellulose (NC) based inks, polyvinyl butyrate (PVB) based inks, polyurethane (PUR) based inks, cellulose acetate propionate (CAP) based inks, polyvinyl chloride (PVC) based inks, polyamide (PA) based inks, water based inks.

[027] The composition of such inks is described in more detail in "The Printing Ink Manual", 5<sup>th</sup> edition, edited by R.H. Leach *et al.*, published by Chapman & Hall in 1993, the disclosure of which is incorporated herein by reference. It will be appreciated that inks, by their very nature, necessarily include at least one pigment.

[028] The laser sensitive material may also be applied as part of an essentially transparent pigment-free coating. The formulation of these coatings is essentially similar to that of the inks, but with the coloured pigment absent.

[029] Whether the laser sensitive material is incorporated into an ink or into a non-pigmented coating, it is preferably present in an amount from 1 to 40%, more preferably from 5 to 20%, and most preferably from 10 to 15% by weight of the whole composition.

[030] Examples of compositions which may be used in the present invention are given in the following Table 1 (inks) and Table 2 (pigment-free coatings), in which the laser sensitive material referred to may be any of the laser sensitive materials mentioned above.

Table 1

	NC based ink	NC based ink 2	PVB based ink	CAP based ink	PVC based ink
NC	10	12			
Polyvinyl butyral			10		
Polyvinyl methyl ether			5		
Polyvinylidene chloride					12
Cellulose acetate propionate				9	
Polyamide					
Urethane	6				
Acrylate				5	
Acrylic Solution					
Acrylic Emulsion					
Styrene-Acrylic-Copolymer-Emulsion					
Defoamer					
Levelling agent					
Dispersing agent	2	2	2	2	2
Adhesion promoter	1				
Monomeric Plasticiser	3	5			
Shellac					
Pigment	20	20	20	20	20
Ethyl acetate	21.5	20.5		11.5	44
Ethanol	21.5	20.5	45	34.5	
Isopropanol					
n-Heptane					
Water					
Laser sensitive Additive	15	20	18	18	22
Total	100	100	100	100	100



Table 1 (cont.)

	PA based ink	Water based ink 1	Water based ink 2	Water based ink 3
NC				
Polyvinyl butyral				
Polyvinyl methyl ether				
Polyvinylidene chloride				
Cellulose acetate propionate				
Polyamide	30			
Urethane				
Acrylate				
Acrylic Solution		50		
Acrylic Emulsion			50	
Styrene-Acrylic-Copolymer-Emulsion		0.5	0.5	1
Defoamer		3	3	1
Levelling agent	2	2	2	2
Dispersing agent				
Adhesion promoter				
Monomeric Plasticiser				20
Shellac	20	15	15	15
Pigment				
Ethyl acetate				
Ethanol	17.25			
Isopropanol	5.75			
n-Heptane		19.5	14.5	51
Water	25	10	15	10
Laser sensitive Additive		100	100	100
Total	100	100	100	100

Table 2

	NC based coating 1	NC based coating 2	NC based coating 3	PVB based coating	CAP based coating
NC	10	8	5		
Polyvinyl butyral				15	
Polyvinyl methyl ether			5		
Polyvinylidene chloride					9
Cellulose acetate propionate					
Polyamide					
Urethane	6				
Acrylate		5			5
Acrylic Solution					
Acrylic Emulsion					
Styrene-Acrylic-Copolymer-Emulsion					
Defoamer					
Levelling agent					
Dispersing agent					
Adhesion promoter	1				
Monomeric Plasticiser					
Shellac			15		
Pigment					
Ethyl acetate	36.5	25	17		15
Ethanol	36.5	50	51	77	61
Isopropanol					
n-Heptane					
Water					
Laser sensitive Additive	10	12	7	8	10
Total	100	100	100	100	100

Table 2 (cont.)

	PVC based coating	PA based coating	Water based coating 1	Water based coating 2	Water based coating 3
NC					
Polyvinyl butyral					
Polyvinyl methyl ether					
Polyvinylidene chloride	12				
Cellulose acetate propionate					
Polyamide		30			
Urethane					
Acrylate					
Acrylic Solution			59	59	
Acrylic Emulsion			22.5		
Styrene-Acrylic-Copolymer-Emulsion				22.5	
Defoamer			0.5	0.5	0.5
Levelling agent			3	3	4
Dispersing agent					
Adhesion promoter					
Monomeric Plasticiser					
Shellac					30
Pigment					
Ethyl acetate	83				
Ethanol					
Isopropanol		41.25			
n-Heptane		13.75			
Water			5	6	55.5
Laser sensitive Additive	5	15	10	9	10
Total	100	100	100	100	100

[031] There is no particular restriction on the nature of the plastic film used as the substrate in the process of the present invention, and any plastic materials commonly used in the industry, especially for food wrapping, may be used. Examples of such materials include synthetic and semi-synthetic organic polymers, such as cellulose acetate, cellulose acetate butyrate (CAB), cellophane, polyvinyl chloride (PVC), polyvinyl fluoride, polyvinylidene chloride (PVDC), polyethylene, polypropylene (PP), polyamides, polyesters, polyphenylene oxide, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polymethyl methacrylate, poly(methyl pentene (TPX), polyvinyl acetal, polystyrene, acrylonitrile-butadiene-styrene (ABS), acrylonitrile-styrene-acrylate (ASA), polycarbonate, polystyrene, polyether sulphone, polyether ketones, polyimides, and copolymers and/or mixtures thereof. If desired, films made from any of these polymers may be coated with coating materials well known in the art, and/or may be laminated to a film or films made of the same or different polymers. Further examples of such plastic materials may be found in standard reference texts, such as "Plastic Films", 3rd Edition, by J. H. Briston, published by Longman Group in 1989.

[032] If desired, the substrate may be coated with a colouring layer impervious to the laser radiation, so as to provide a layer of a contrasting colour to that of the ink subsequently applied. When the ink is removed by thermal action in accordance with the process of the invention, the lower, laser-impervious, layer will be seen as a contrasting colour and will form the printed markings generated by the laser. Alternatively, the coating layer of ink which is selectively removed may be coloured, so that, when it is removed, the native colour of the substrate is seen as a contrast.

[033] Once the ink has been applied to the substrate comprising the flexible plastic film, it is cured or dried to form a coherent layer on the substrate. If desired, one or more further films of plastic material may be laminated to the coated substrate. This may be any of the polymers listed above, but should be transparent to the radiation of the laser employed. If another film is laminated on top of the ink, and the ink emits gases or otherwise undergoes an increase in volume on being heated by the heat resulting from absorption of the laser energy by the laser sensitive material, the portion of the laminated film above the markings will be raised, thus giving an embossed effect which otherwise would be difficult to achieve and which can be very desirable.

[034] The present invention can thus provide thin flexible plastic films which may be coated in many ways. Examples of these include:

1. The film may be coated with a single layer of an ink containing the laser sensitive material;
2. The film may be coated with a layer of laser sensitive material, which, in turn, is coated with a layer of ink;
3. The film may be coated with a layer of ink, which, in turn, is coated with a single layer of an ink containing the laser sensitive material;
4. The film may be coated with a layer of ink, which, in turn, is coated with a layer of laser sensitive material, that being coated with a layer of ink.

[035] In general terms, we prefer that either the laser sensitive material is mixed with the ink or that the ink and the laser sensitive material are in separate, but associated, layers, the layer of ink to be removed by the process of the present invention being on the side of the layer of laser sensitive material remote from the substrate.

[036] Any of the above may be coated with further layers of material, for example, varnish, provided that any such further layers are transparent or essentially transparent, to the laser radiation. Moreover, if desired, the film may be coated with one or more other layers of materials, such as inks, varnishes and the like, prior to being coated with the first layer in accordance with the present invention.

[037] In the embodiment of the present invention where a laser sensitive material is or is associated with a material which evolves gas when heated, it may be the laser sensitive material which evolves gas. Alternatively, the laser sensitive material may be associated with, e.g. mixed with, another material which evolves gas. The material is then coated with a gasimpermeable layer, which can be any such known material. As a result, when exposed to laser radiation, the exposed portions emit a gas. However, this is trapped by the coating layer, and, as a result, forms minute bubbles under the coating layer. These can be perceived both by the eye and by touch and give a desirable embossed appearance, suitable for Braille or Moon script.

[038] The present invention is further illustrated by the following non-limiting Examples.

#### Example 1

[039] A laser sensitive solvent based coating was printed on transparent oriented polypropylene (OPP) film, and then overprinted with a nitrocellulose based cyan ink. The formulation of the laser sensitive coating was (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	11
Ethyl acetate	22
Ethanol	32
Methoxypropanol, Dowanol PM ex Dow	15
Plasticiser Plastifiant 1026 ex SNPE	10
Iriodin LS 825 ex Merck	10
Total	100

The cyan ink was Europa cyan ex Sun Chemical. After exposure to a Nd:YAG laser, marks were visible as a result of removal of the cyan ink from the regions exposed to the laser beam.

**Example 2**

[040] A laser sensitive solvent based coating was printed on transparent OPP film, and then overprinted with a nitrocellulose based cyan ink. The formulation of the laser sensitive coating was

5 (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	11
Ethyl acetate	22
Ethanol	32
Methoxypropanol, Dowanol PM ex Dow	15
Plasticiser Plastifiant 1026 ex SNPE	10
Iridin LS 800 ex Merck	10
Total	100

The cyan ink was Europa cyan ex Sun Chemical. After exposure to a CO<sub>2</sub> laser, marks were visible as a result of removal of the cyan ink from the regions exposed to the laser beam.

10

**Example 3**

[041] A laser sensitive solvent based coating was printed on transparent OPP film, and then overprinted with a nitrocellulose based cyan ink. The formulation of the laser sensitive coating was

15 (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	36.5
Ethanol	36.5
Urethane, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter Lutonal M40 ex BASF	1.0
Kaolin	10.0
Total	100.0

The cyan ink was Europa cyan ex Sun Chemical. After exposure to a CO<sub>2</sub> laser, marks were visible as a result of removal of the cyan ink from the regions exposed to the laser beam.

**Example 4**

[042] A laser sensitive solvent based coating was printed on transparent OPP film, and then overprinted with a nitrocellulose based cyan ink. The formulation of the laser sensitive coating was

5 (parts by weight):

Polyvinyl butyral, Pioloform BN18 ex Wacker	15
Ethanol	75
Iriodin LS 825 ex Merck	10
Total	100

The cyan ink was Europa cyan ex Sun Chemical. After exposure to a Nd:YAG laser, marks were visible as a result of removal of the cyan ink from the regions exposed to the laser beam.

10

**Example 5**

[043] A laser sensitive water based coating was printed on transparent OPP film, and then overprinted with a nitrocellulose based cyan ink. The formulation of the laser sensitive coating was (parts by weight):

15

Acrylic Solution Joncryl 678 ex Johnson	59.0
Acrylic Emulsion Joncryl 80 ex Johnson	22.5
Water	5.0
Defoamer TPE714 ex Henkel	0.5
Levelling agent Surfynol SE-F ex Air Products	3.0
Iriodin LS 825 ex Merck	10.0
Total	100.0

The cyan ink was Europa cyan ex Sun Chemical. After exposure to a Nd:YAG laser, marks were visible as a result of removal of the cyan ink from the regions exposed to the laser beam.

EExample 6

[044] A laser sensitive solvent based coating was printed on transparent OPP film, and then overprinted with a nitrocellulose based yellow ink. The formulation of the laser sensitive coating

5 was (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	11
Ethyl acetate	17
Ethanol	27
Methoxypropanol, Dowanol PM ex Dow	15
Plasticiser Plastifiant 1026 ex SNPE	10
Iriodin LS 800 ex Merck	10
Iriodin LS 825 ex Merck	10
Total	100

The cyan ink was Europa yellow ex Sun Chemical. After exposure to a Nd:YAG or CO<sub>2</sub> laser, marks were visible as a result of removal of the cyan ink from the regions exposed to the laser beam.

10

Example 7

[045] A nitrocellulose based white ink was printed on transparent polyethylene terephthalate (PET), and was overprinted with a solvent based laser sensitive magenta ink. The formulation of the laser sensitive magenta ink was (parts by weight):

15

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	18.5
Ethanol	18.5
Methoxypropanol, Dowanol PM ex Dow	10.0
Urethane resin, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Plasticiser, Dioctyl phthalate ex BASF	3.0
Magenta pigment, Symular Brilliant 363SD ex DIC	18.0
Iriodin LS 825 ex Merck	15.0
Total	100.0



The white ink was Europa white ex Sun Chemical. After exposure to a Nd:YAG laser, marks were visible as a result of removal of the magenta ink from the regions exposed to the laser beam, while the white ink film had not been removed by the laser.

5

### Example 8

[046] A cellulose acetate propionate based orange ink was printed on transparent polypropylene (PP), and then overprinted with a solvent based laser sensitive coating, which, in turn, was overprinted with cellulose acetate propionate based green ink. The formulation of the laser sensitive coating was (parts by weight):

10

Nitrocellulose, Nitro CA4 A15 ex Bergerac	11
Ethyl acetate	22
Ethanol	32
Methoxypropanol, Dowanol PM ex Dow	15
Plasticiser Plastifiant 1026 ex SNPE	10
Iriodin LS 825	10
Total	100

The orange ink was Europa orange ex Sun Chemical. The green ink was Europa green ex Sun Chemical. After exposure to a Nd:YAG laser, marks were visible since the orange ink was not removed by the laser and gave contrast to the green ink which had been removed.

15

### Example 9

[047] A polyvinyl butyral based laser sensitive coating was printed on PET and overprinted with a polyvinyl butyral based red ink. This film was laminated with a two-pack adhesive onto polyethylene (PE). The formulation of the laser sensitive coating was (parts by weight):

20

Polyvinyl butyral Pioloform BN18 ex Wacker	15
Ethanol	75
Iriodin LS825	10
Total	100

The red ink was Optiprint red ex Sun Chemical. The adhesive was Mor-Free 402A/Mor-Free C79 ex Rohm & Haas. After exposure to a Nd:YAG laser, marks were visible as a result of removal (or change in colour) of the red ink from the regions exposed to the laser beam.

5

### Example 10

[048] A nitrocellulose based white ink printed on PET was overprinted with a nitrocellulose based laser sensitive coating and a polyvinyl butyral based yellow ink. This film was laminated with a two-pack solvent free adhesive onto PP. The formulation of the laser sensitive coating was (parts by weight):

10

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	36.5
Ethanol	36.5
Urethane, Surkopak SE-F ex SNPE	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Iriodin LS 825	10.0
Total	100.0

The white ink was Europa white ex Sun Chemical. The yellow ink was Optiprint yellow ex Sun Chemical. The solvent based adhesive was Herberts EPS71-72 / KS65 ex Herberts. After exposure to a Nd:YAG laser, marks were visible as a result of removal of the yellow ink from the regions exposed to the laser beam.

15

### Example 11

[049] A nitrocellulose based laser sensitive green was printed on polyamide (PA). The formulation of the laser sensitive green ink was (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	18.5
Ethanol	18.5
Methoxypropanol, Dowanol PM ex Dow	10.0
Urethane resin, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Plasticiser, Dioctyl phthalate ex BASF	3.0
Green pigment, Sunfast green 264-5504 ex Sun Chemical	18.0
Iriodin LS 825 ex Merck	15.0
Total	100.0

20

After exposure to a Nd:YAG laser, marks were visible as a result of removal of the green ink from the regions exposed to the laser beam.

### Example 12

- 5        [050] A nitrocellulose based laser sensitive blue ink was printed on PA. The formulation of the laser sensitive blue ink was (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	18.5
Ethanol	18.5
Methoxypropanol, Dowanol PM ex Dow	10.0
Urethane resin, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Plasticiser, Dioctyl phthalate ex BASF	3.0
Blue pigment, Fastogen Blue 5412 SD ex DIC PBI 15:4	18.0
Iriodin LS 800 ex Merck	15.0
Total	100.0

- 10        After exposure to a CO<sub>2</sub> laser, marks were visible as a result of removal of the blue ink from the regions exposed to the laser beam.

### Example 13

- 15        [051] A polyvinyl butyral based laser sensitive blue ink was printed on PA. The formulation of the laser sensitive blue ink was (parts by weight):

Polyvinyl butyral, Pioloform BN18 ex Wacker	10.0
Adhesion promoter, Lutonal M40 ex BASF	5.0
Ethanol	52.0
Blue pigment, Heliogen blue 7086 ex BASF, PBI 15:3	18.0
Iriodin LS 800 ex Merck	15.0
Total	100.0

After exposure to a CO<sub>2</sub> laser, marks were visible as a result of removal of the blue ink from the regions exposed to the laser beam.

**Example 14**

[052] A water based laser sensitive blue ink was printed on PA. The formulation of the laser sensitive blue ink was (parts by weight):

5

Acrylic Emulsion, Joncryl 80 ex Johnson	50.0
Water	14.5
Defoamer TPE714 ex Henkel	0.5
Levelling agent, Surfynol SE-F ex Air Products	3.0
Pigment, Meghfast Blue BD909 ex Meghmani, PB1 15:3	17.0
Iriodin LS 825 ex Merck	15.0
Total	100.0

After exposure to a Nd:YAG laser, marks were visible as a result of removal of the blue ink from the regions exposed to the laser beam.

10

**Example 15**

[053] A nitrocellulose based laser sensitive yellow ink was printed on PA. The formulation of the laser sensitive yellow ink was (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	16.0
Ethanol	16.0
Methoxypropanol, Dowanol PM ex Dow	10.0
Urethane resin, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Plasticiser, Dioctyl phthalate ex BASF	3.0
Yellow pigment Permanent yellow P-GRL06 ex Clariant	18.0
Iriodin LS 825 ex Merck	10.0
Iriodin LS 800 ex Merck	10.0
Total	100.0

15 After exposure to a Nd:YAG or CO<sub>2</sub> laser, marks were visible as a result of removal of the blue ink from the regions exposed to the laser beam.

**Example 16**

[054] A laser sensitive nitrocellulose based orange ink was printed on PET. The film was laminated with a two-pack adhesive onto PE. The formulation of the laser sensitive orange ink was

5 (parts by weight):

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	18.5
Ethanol	18.5
Methoxypropanol, Dowanol PM ex Dow	10.0
Urethane resin, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Plasticiser, Dioctyl phthalate ex BASF	3.0
Orange pigment, Diacetanil orange 3426C ex Cappelle	18.0
Iriodin LS 825 ex Merck	15.0
Total	100.0

The adhesive was Mor-Free 402A/Mor-Free C79 ex Rohm & Haas. After exposure to a Nd:YAG laser, marks were visible as a result of removal of the orange ink from the regions exposed to the

10 laser beam.

**Example 17**

[055] A polyvinyl butyral based white ink was printed on PE, and was overprinted with laser sensitive polyvinyl butyral based violet ink. This film was laminated with water based adhesive on

15 PP. The formulation of the laser sensitive violet ink was )parts by weight):

Polyvinyl butyral, Pioloform BN18 ex Wacker	10
Adhesion promoter, Lutonal M40 ex BASF	5
Ethanol	53
Blue pigment, Heliogen blue BD909 ex BASF	17
Iriodin LS 825	15
Total	100

The white ink was Europa white ex Sun Chemical. The water based adhesive was Aqua-LAM 300A/Aquabond 444C ex Rohm & Haas. After exposure to a Nd:YAG laser, marks were visible as a result of removal of the violet ink from the regions exposed to the laser beam.

5.

**Example 18**

[056] A laser sensitive water based coating was printed on a transparent OPP film, and was then overprinted with a water based, irreversible, thermochromic ink. The formulation of the laser sensitive coating was:

Acrylic Solution, Joncryl 678 ex Johnson	59.0
Acrylic Emulsion, Joncryl 80 ex Johnson	22.5
Water	5.0
Defoamer TPE714 ex Henkel	0.5
Levelling agent, Surfynol SE-F ex Air Products	3.0
Iriodin LS 825 ex Merck	10.0
Total	100.0

- 10 The thermochromic ink was a water based flexo ink ex Sun Chemical with irreversible colour change at 90 °C from colourless to dark grey. After exposure to a NdYAG laser, marks were visible as a result of irreversible colour change of the thermochromic ink, due to energy absorption in the laser sensitive coating and temperature increase to more than 90 °C. The laser power has to be in a range such that there is enough energy to reach the recommended temperature for the colour change but not
- 15 to remove the ink layer.

**Example 19**

- [057] A laser sensitive solvent based coating was printed on shrinkable PET film, and was then overprinted with a nitrocellulose based white ink. The film was shrunk on a glass bottle where
- 20 the printed side has contact with the bottle. The formulation of the laser sensitive coating was:

Polyvinylbutyral, Pioloform BN18 ex Wacker	15
Ethanol	75
Iriodin LS 825 ex Merck	10
Total	100

The white ink was Europa white ex Sun Chemical. After exposure to a NdYAG laser, dark marks were visible as a result of removal of the white ink from the regions of the film exposed to the laser beam. The ink was transferred to the surface of the bottle, so a copy of the marks was visible after removal of the film. This can be used as a security characteristic.

5

#### Example 20

[058] A nitrocellulose based laser sensitive blue ink was printed on shrinkable PET. The film was shrunk on a PET bottle where the printed side was in contact with the bottle. The formulation of the laser sensitive blue ink was:

10

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	18.5
Ethanol	18.5
Methoxypropanol, Dowanol PM ex Dow	10.0
Urethane resin, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Plasticiser, Dioctyl phthalate ex BASF	3.0
Blue pigment, Fastogen Blue 5412 SD ex DIC PBI 15:4	18.0
Iriodin LS 800 ex Merck	15.0
Total	100.0

After exposure to a CO<sub>2</sub> laser, marks were visible as a result of removal of the blue ink from the regions exposed to the laser beam. The ink was transferred to the surface of the bottle, so a copy of the marks was visible after removal of the film. This can be used as a security characteristic.

15

**Example 21**

[059] A laser sensitive solvent based coating was printed on transparent OPP film, and was then overprinted with a nitrocellulose based cyan ink. The same coating layers were applied to paper. The printed film over-wrapped the printed paper. The formulation of the laser sensitive coating was:

Nitrocellulose, Nitro CA4 A15 ex Bergerac	11
Ethyl acetate	22
Ethanol	32
Plasticiser, Plastifiant 1026 ex SNPE	10
Methoxypropanol, Dowanol PM ex Dow	15
Iriodin LS 825 ex Merck	10
Total	100

The cyan ink was Europa cyan ex Sun Chemical. The laser exposure was partly on film and partly on paper. After exposure to a NdYAG laser, marks were visible as a result of removal of the cyan ink from the regions of the film and the paper exposed to the laser beam. This can be used as a security characteristic.

**Example 22**

[060] A nitrocellulose based yellow ink was printed on polyvinyl acetal film as micro text. It was then overprinted with a solvent based laser sensitive blue ink. The formulation of the laser sensitive blue ink was:

Nitrocellulose, Nitro CA4 A15 ex Bergerac	10.0
Ethyl acetate	18.5
Ethanol	18.5
Methoxypropanol, Dowanol PM ex Dow	10.0
Urethane resin, Surkopak 5244 ex Tennants Inks	6.0
Adhesion promoter, Lutonal M40 ex BASF	1.0
Plasticiser, Dioctyl phthalate ex BASF	3.0
Blue pigment, Fastogen Blue 5412 SD ex DIC PB1 15:4	18.0
Iriodin LS 800 ex Merck	15.0
Total	100.0



The yellow ink was Europa yellow ex Sun Chemical. After exposure to a CO<sub>2</sub> laser, marks were visible as a result of removal of the blue ink from the regions exposed to the laser beam. Inside the marks, formed by the removal of the blue ink, the yellow micro text underneath was visible. This can be used as a security characteristic.

5

### Example 23

[061] A nitrocellulose based yellow ink was printed on transparent OPP film as micro text. It was then overprinted with a laser sensitive solvent based coating which was overprinted with a nitrocellulose based cyan ink. The formulation of the laser sensitive coating was:

10

Nitrocellulose, Nitro CA4 A15 ex Bergerac	11
Ethyl acetate	22
Ethanol	32
Plasticiser, Plastifiant 1026 ex SNPE	10
Methoxypropanol, Dowanol PM ex Dow	15
Iriodin LS 825 ex Merck	10
Total	100

The yellow ink was Europa yellow ex Sun Chemical, the cyan ink was Europa cyan ex Sun Chemical. After exposure to a CO<sub>2</sub> laser, marks were visible as a result of removal of the blue ink from the regions exposed to the laser beam. In the marks, formed by the removal of the blue ink, the yellow micro text underneath was visible. This can be used as a security characteristic.

15

### Example 24

[062] A polyvinyl butyral based laser sensitive coating was printed on PE. This film was laminated onto PET using a 2-compound adhesive. The formulation of the laser sensitive coating was:

20

Polyvinylbutyral, Pioloform BN18 ex Wacker	15
Ethanol	75
Iriodin LS825	10
Total	100.0

After exposure to a NdYAG laser, marks were visible and tangible as a result of bubbles, formed in between the two plastic films, caused by the thermal destruction of the laser sensitive coating. The intensity of bubble formation can be influenced by the laser power. These marks can also be felt by blind people. They can, therefore, be used as Braille or Moon script.

**CLAIMS:**

1. A process for marking a flexible plastic material using a laser, which process comprises the steps: applying to a surface of a substrate comprising said flexible plastic material in one or more layers an ink in association with a laser sensitive material; drying the ink; exposing portions of the ink to laser radiation at a wavelength to which said laser sensitive material is sensitive so that laser radiation absorbed by the laser sensitive material heats and removes thermally the ink or causes the ink to change colour, so as to cause markings to appear on the exposed portions.
2. A process according to Claim 1, in which said laser sensitive material is applied to the substrate and then a layer of said ink is applied over the laser sensitive material.
3. A process according to Claim 1, in which said ink contains said laser sensitive material.
4. A process according to any one of Claims 1 to 3, in which heating removes the ink.
5. A process for marking a flexible plastic material using a laser, which process comprises the steps: applying to a surface of a substrate comprising said flexible plastic material a laser sensitive material which is or is associated with a material that generates gas on heating; coating the laser sensitive material with a gas-impermeable layer; exposing portions of the laser sensitive material to laser radiation at a wavelength to which said laser sensitive material is sensitive so that laser radiation absorbed by the laser sensitive material heats and causes gas to be generated, so as to form raised markings to appear on the exposed portions.
6. A process according to any one of Claims 1 to 5, in which said laser is a CO<sub>2</sub> laser.
7. A process according to Claim 6, in which said laser sensitive material is mica, metal oxide-coated mica particles, aluminium powder, carbon black, kaolin or another silicate, titanium dioxide or calcium carbonate.
8. A process according to any one of Claims 1 to 5, in which said laser is an Nd:YAG laser.
9. A process according to Claim 8, in which said laser sensitive material is mica, metal oxide-coated mica particles, aluminium powder, carbon black, titanium dioxide or calcium carbonate.

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(54) Title: **LASER MARKING PROCESS**

(57) Abstract: Thin, flexible plastic films, of the type used for the packaging of foodstuffs, may be printed using a laser marking technique by printing a layer or layers comprising a laser sensitive material and an ink so that heating of the laser sensitive material by absorption of laser radiation burns the ink selectively, so causing markings to appear. A further process for marking a flexible plastic material using a laser is disclosed, whereby to a surface of a substrate comprising said flexible plastic material a laser sensitive material which is or is associated with a material that generates gas on heating is applied, this is coated with a gas impermeable layer, then exposed to laser radiation such that raised markings appear on the exposed portions.

# INTERNATIONAL SEARCH REPORT

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**A. CLASSIFICATION OF SUBJECT MATTER**

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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